C. Postshred Materials Recovery Technology Development and Demonstration

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The Association of Plastics Manufacturers of Europe provided cost-sharing for the Salyp NV process evaluation.
Changing World Technologies is cost-sharing on the evaluation of their thermal depolymerization process.
The Polyurethanes Recycle and Recovery Council (PURCC) is also participating and cost-sharing on the evaluation of the Troy Polymers, Inc., polyurethane glycolysis process.

Contractor: Argonne National Laboratory
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Objective

- Develop and demonstrate technology for the cost-effective recovery of materials from postshred residues.

Approach

- Characterize shredder residues from a number of sources to determine composition variability.
- Conduct bench-scale and large-scale process/technology tests to benchmark technology.
- Build and operate a shredder residue separation pilot plant to produce samples of recovered materials for market evaluation.
- Conduct costs and performance analysis of alternative technologies to establish the business case for the technologies and to identify technology gaps.

Accomplishments

- Completed characterization of five shredder residues; two European and three United States.
- Completed large-scale tests of Salyp's "thermoplastics sorting" technology using residue from two European and one U.S. location as feed materials.

- Completed construction in the first quarter of FY 2004 of a large-scale pilot separation facility at Argonne National Laboratory; shakedown of the facility occurred during the second and third quarter, production campaigns have been started.
- Completed bench-scale testing of Changing World Technologies (CWT) thermal depolymerization process; test runs have been initiated using 3000 lb of bulk shredder residue.
- Started bench-scale testing of a glycolysis process for conversion of polyurethane foam to polyol initiators.
- Developed an Excel-based process cost model that incorporates two primary modules for recovery of automotive plastics: the first module includes the unit operations required for recovering a plastics concentrate from shredder residues, and the second module includes the unit operations required to recover selected plastics from the mixed plastics concentrates.

Future Direction

- Continue characterization of shredder residue.
- Complete CWT thermal depolymerization tests; evaluate process economics; define path forward.
- Complete Polyventure/TPI glycolysis bench-scale tests; evaluate process performance; define path forward.
- Complete Argonne froth flotation campaigns, evaluate process performance and economics; define path forward.
- Update process cost analysis model.
- Review/critique technology developments with representatives of the automotive shredding industry.

Summary

The objective of this project is to develop and demonstrate technology for the cost-effective recovery of materials from postshred residues.

A wide range of materials recovery technologies is at various stages of development. Certain of those technologies specific to recovery of materials from postshred materials streams will be evaluated and demonstrated to fully understand the commercial viability of those processes.

The objective of this project is to determine the performance (e.g., yield, purity, efficiency, and cost) of these emerging technologies such that an optimized and integrated process for recovering these materials from shredder residue can be developed.

Research conducted in this project will provide data essential to establishing a business case for sustained recycling of automotive materials from postshred residue.

Research has been completed on the Salyp N.V. physical separation/thermosorting process. Research is ongoing on the Argonne physical separation/froth flotation process, the Changing World Technologies (CWT) thermal depolymerization process, and The Polyventure/Troy Polymers process for glycolysis of polyurethane foam.

Characterization of Shredder Residue

To facilitate the development of technology for recovery of materials and resources from shredder residue, characterization of shredder residue from different sources has been conducted by MBA Polymers. Small (2-kg) samples of shredder residue from five sources have been characterized to date: two European and three American. Samples of shredder residue from other sources will be analyzed as appropriate throughout the course of the project.

In general, while there are some differences in the composition of the shredder residue from each source, the differences do not yet appear to be significant in terms of the design constraints of recovery technology. The bulk composition of the residue samples is compared in Table 1. The composition of the plastics fraction for each sample is compared in Table 2.

Table 1. Bulk composition of European and U.S. shredder residue (*Basis*: small sample, ~1 kg, analysis)

Materials	Europe 1	Europe 2	U.S. 1	U.S. 2	U.S. 3
Fines (<1/8 in.)	18.0	4.9	37.5	32.8	5.3
Residual metals	3.0	6.4	9.3	7.1	15.5
Foam	36.8	31.6	21.3	26.6	26.9
Wood	0.4	3.2	7.2	4.0	1.9
Rubber	17.3	22.5	4.9	9.3	27.7
Stone, fiber, other	10.1	0.0	7.4	8.9	5.5
Plastics	14.4	31.4	12.4	11.3	17.2

Table 2. Composition of the plastics fraction of European and U.S. shredder residue (*Basis*: small sample, ~1 kg, analysis)

Plastic	Europe 1	Europe 2	U.S. 1	U.S. 2	U.S. 3
Polypropylene	41.4	31.9	26.3	41.0	33.3
Polyethylene	3.7	17.3	6.6	7.0	5.3
High-impact PS	4.9	3.3	25.9	15.2	28.1
ABS	8.8	11.5	17.1	22.2	11.8
PA	11.8	2.1	2.9	3.7	10.7
PVC	0.7	10.4	0.0	0.0	1.9
Rigid urethane	18.9	13.4	4.1	0.5	4.1
PC/PBT	6.6	4.2	1.9	2.7	4.4
Other	3.2	5.9	15.2	7.6	5.7

Argonne Pilot Plant

Construction of the pilot plant at Argonne was completed in the first quarter of FY 2004. The facility will be used to

1. conduct optimization/integration studies,
2. provide a production capability to produce large samples of recovered materials for market evaluation,
3. demonstrate the effectiveness of alternative separation technologies and systems, and
4. serve as a user/demonstration facility to conduct separation tests for residue from specific sources.

The pilot plant consists of two major unit operations. The first is a mechanical separation facility; the second is a wet-density/froth-flotation separation facility.

The mechanical separation facility is shown schematically in Figure 1. An overview of the facility is shown in Figure 2. The mechanical separation facility processes the raw shredder residue to yield a "plastics concentrate." The raw shredder residue is separated into the following fractions:

- oversize tramp material,
- fines (–5/16 in.),
- oversize [polyurethane foam (PUF), fiber, etc.],
- nonferrous,
- ferrous,
- small fluff and other light materials,
- other reject, and
- middling/plastics concentrate.

The "middling" fraction is further processed for size reduction in a small shredder to produce the plastics concentrate.

The wet density/froth-flotation facility is shown schematically in Figure 3. An overview of this pilot plant is shown in Figure 4. It includes six continuous stages for separation and recovery of targeted materials from the plastics concentrates derived from shredder residue.

The first stage cleans the plastics concentrate and also recovers the lighter olefins for further processing. The second stage drops out heavy

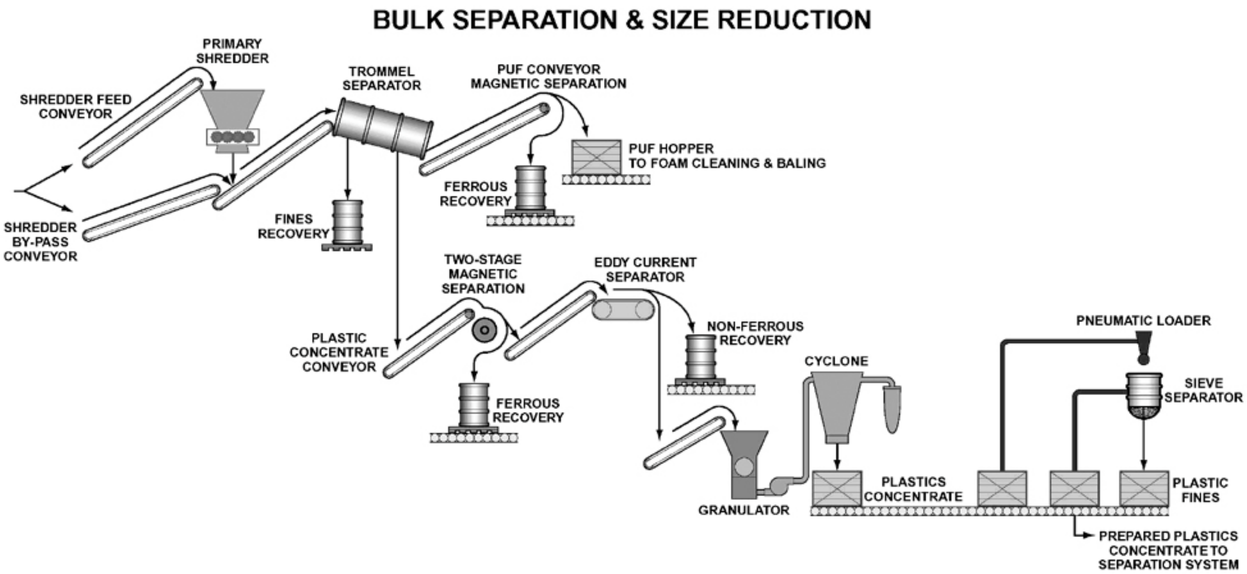

Figure 1. Schematic of the Argonne Pilot Mechanical Separation System for processing raw shredder residue.

Figure 2. Overview of the Argonne Bulk Separation Pilot Plant.

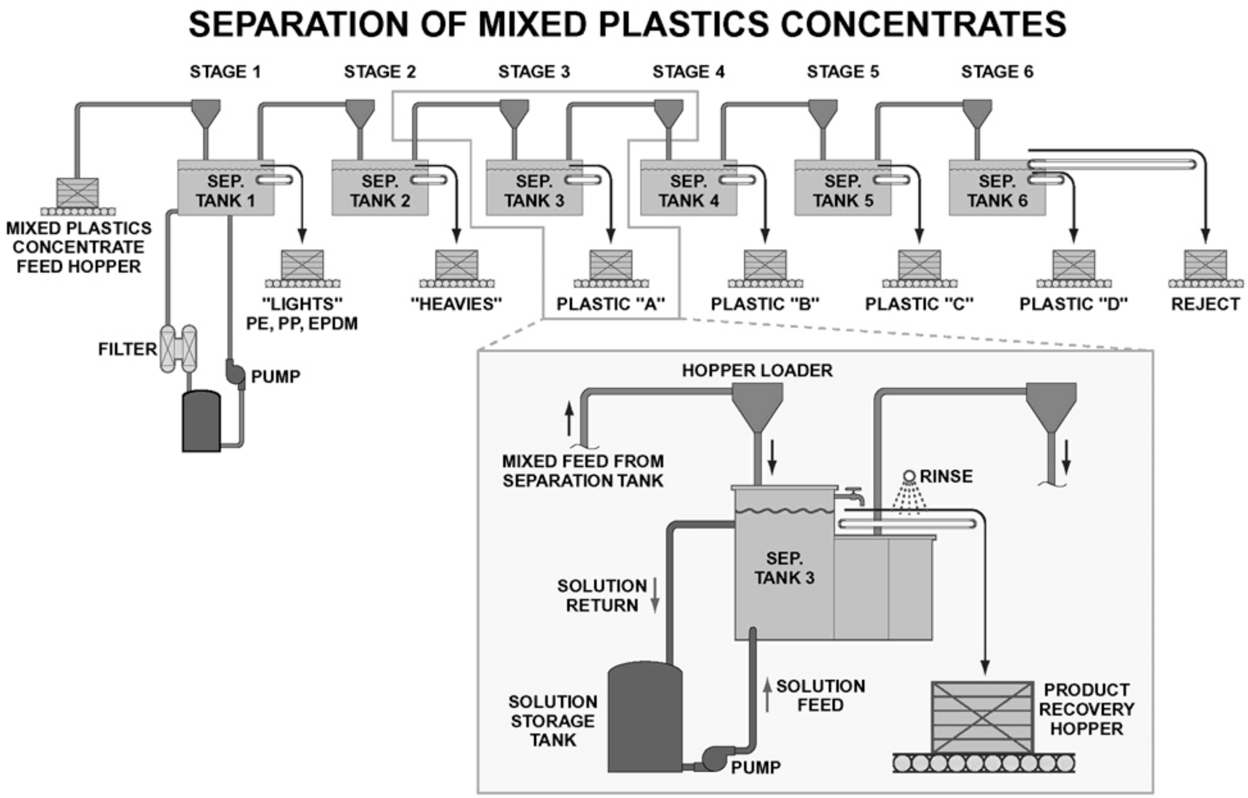

Figure 3. Schematic of the Argonne Pilot Wet Separation System for recovery of plastics from shredder residue.

Figure 4. Overview of the Argonne Froth-Flotation Pilot Plant.

materials, including any residual metals that remain in the concentrate.

The following four stages will process the balance of the concentrate for recovery of the following targeted materials:

- acrilonitrile-batadiene-styrene (ABS),
- high-impact polystyrene (HIPS),
- nylon, and
- polyvinyl chloride (PVC).

Depending on recovery rates and yield, other polymer cuts may be explored to define the overall best strategy for separation and recovery of the materials from the concentrates.

Shakedown of the wet density/froth-flotation facility was conducted during the second quarter of FY 2004. Shakedown was conducted using about 4000 lb of postconsumer electronics and appliance mixed plastics because the composition of these materials is much less variable than the composition of plastics concentrate from shredder residue. The composition of a feed material for the shakedown trials is shown in Figure 5. The shakedown tests were conducted using four of the six froth-flotation stages targeting recovery of the ABS and HIPS from the feed material. In these trials, approximately 75% of the feed material HIPS was recovered in a single fraction at a purity of 97% (Figure 6). The ABS yield was lower at about 55%; however, the purity of the ABS was 98%. Physical properties of the recovered materials were consistent with a range of "virgin" or primary grades of HIPS and ABS,

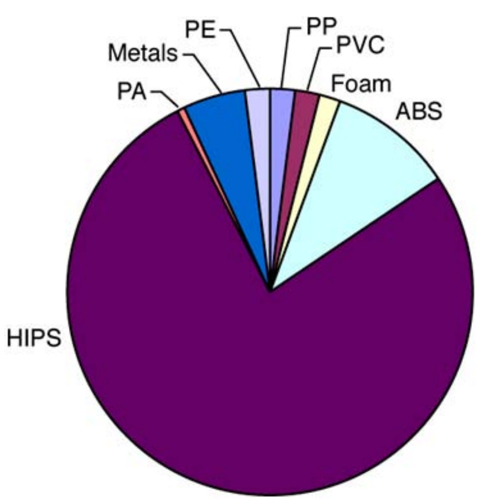

Figure 5. Composition of postconsumer mixed plastics used in Argonne Froth-Flotation Pilot Plant shakedown trials.

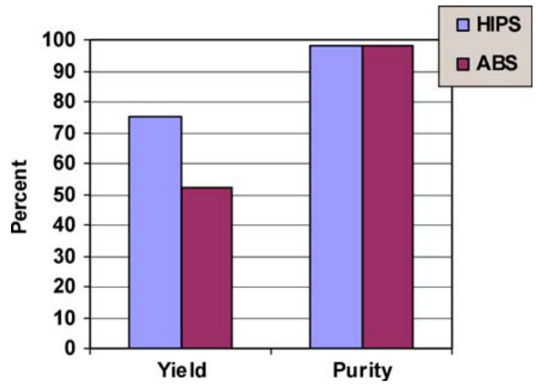

Figure 6. Percentage of HIPS and ABS recovered (yield) and purity of the recovered HIPS and ABS.

respectively. (See Compatibilization/Compounding Evaluation of Recovered Polymers annual report, see 6.E)

Following shakedown of the froth-flotation system, shakedown and debottlenecking of the bulk separation pilot plant was undertaken during the third quarter of FY 2004.

During the fourth quarter, campaigns were undertaken that resulted in the physical/bulk separation of about 60,000 lb of shredder residue (6 campaigns). The average yield of plastics concentrate from these campaigns was about 17% (Figure 7). The composition of the recovered plastics concentrate is, of course, much more complex than the plastics fraction from just appliance or electronics scrap (Figure 8).

The initial froth-flotation campaigns run with the shredder residue plastics concentrate showed that the process could recover a concentrated

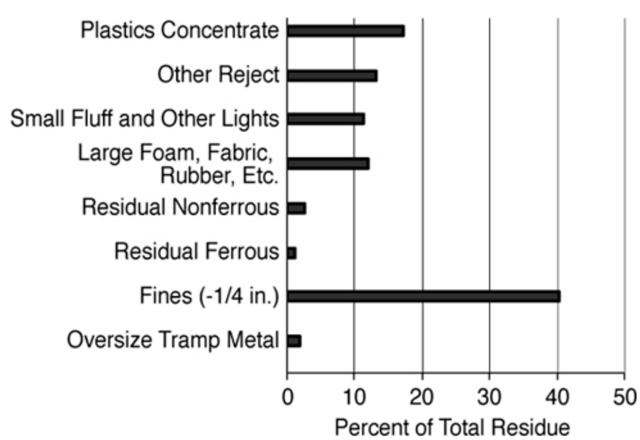

Figure 7. Bulk composition of shredder residue processed in Argonne's Bulk Separation Pilot Plant. (*Basis*: 60,000 lb, six campaigns.)

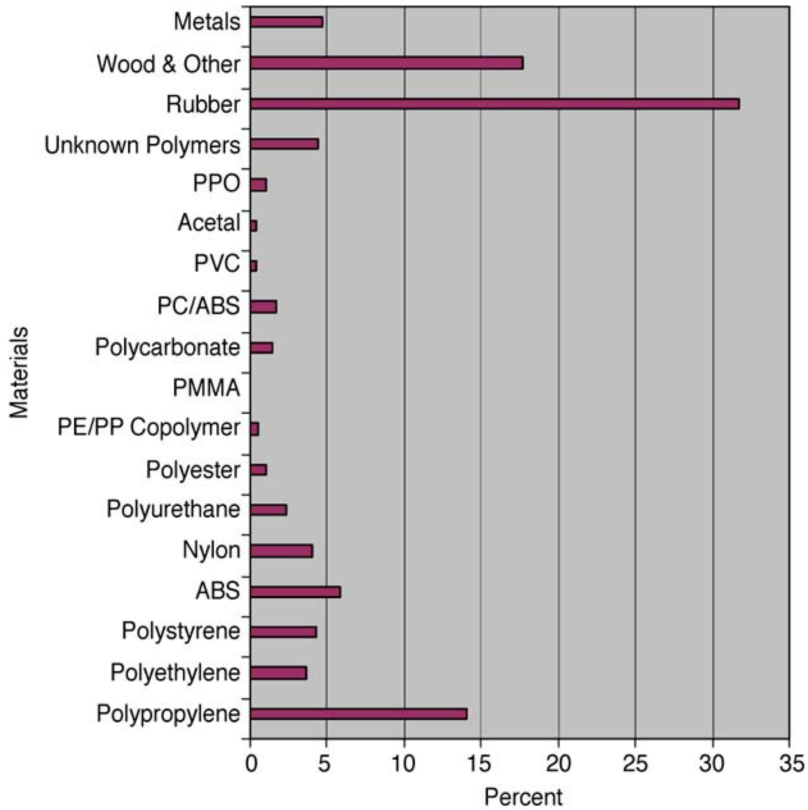

Figure 8. Average composition of the plastics concentrate fraction recovered from shredder residue. (*Basis*: 60,000 lb, six campaigns.)

polyolefin's fraction and a concentrated ABS fraction, but that these materials contained a significant amount of residual wood and rubber. The effectiveness of the froth-flotation process is dependent on the ability to isolate these materials from the balance of the plastics concentrate. The technical feasibility of conventional separation equipment such as gravity tables, mineral jigs, and hydrocyclones in isolating the wood and rubber from the plastics concentrate will be evaluated as the research on mechanical separation continues. Alternative operating conditions for the froth-flotation system are also being evaluated.

Salyp Thermo-Plastics Sorting Technology

Salyp N.V., a Belgium company has developed and integrated a full recycling line using different sorting technologies, which processes and recycles various material fractions from shredder residue. The key objective of the project was to determine the feasibility of a mechanically automated, near industrial recovery of various mixed engineering plastics into individual plastic streams.

Salyp processed three different shredder residues totaling 100 metric tons that included one U.S. shredder and two European shredders. Each shredder selected sent approximately 33 metric tons of shredder residue to Salyp for processing.

Results from this study indicated that Salyp was able to separate different material streams that included

- metals,
- fibers,
- foam (using Argonne's technology),
- fines, and
- plastic concentrates.

The economics of shredder residue separation were determined, and the following costs were defined.

- Investment cost for machinery and equipment to process 40,000 tons of shredder residue per year is estimated at $3.6M.
- Cost for separation of a mixed plastic stream is estimated at 13¢/lb.

Salyp's near-industrial sorting line was able to recover a mixed plastics fraction. However, sorting the mixed plastic fraction into individual plastic streams could not be accomplished.

Changing World Technologies

Changing World Technologies, Inc. (CWT) has developed a two-stage thermal conversion process that converts organic material into fuels, gases, and solids. CWT's first commercial facility based on this technology was commissioned in April 2003 and converts 200 tons/d of turkey offal into fuels and fertilizers. This installation is a joint venture partnership with ConAgra and CWT. The thermal conversion process should be able to process the organic materials in shredder residue.

CWT's research and development center is located at the Philadelphia Naval Yard where they have a 7-ton/d pilot plant (Figure 9).

The CRADA team funded a study on a limited basis to CWT titled "Protocol Testing Shredder Residue Project." This study focused on a select sampling of two different types of shredder residue. Results from this initial study indicated that the CWT process was able to convert the shredder residue samples to three product fractions: an oil, a gas, and a carbon char. The resultant oil product characteristics are summarized in Table 3.

Based on the results of this initial project testing, CWT has offered to process 3,000 lb of shredder residue to further confirm the technical and economic feasibility of this process.

At the completion of this study, CWT will prepare a final report for the CRADA team; it will include a Performance Cost Analysis that defines converting plastics from shredder residue into fuels and chemicals. Additionally, the output products will also be made available to the CRADA project members for further analysis and testing.

If the results look promising, the CRADA team will investigate further funding opportunities that will aid in the launch of a scale-up study.

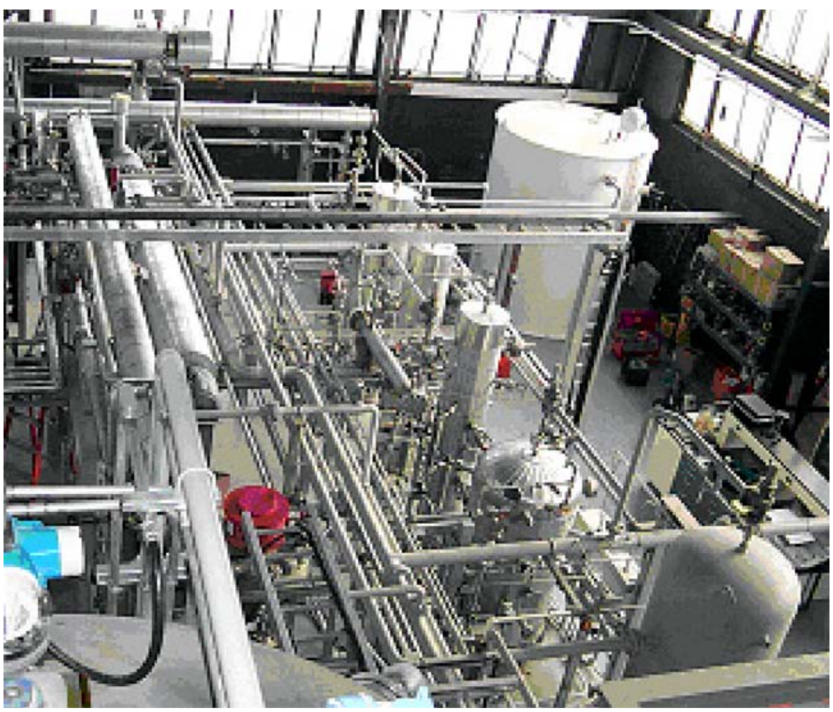

Figure 9. Overview of the CWT Thermal Conversion Pilot Plant.

Table 3. CWT oil characteristics from shredder residue feedstock

Method	Test	SR bucket 1	SR bucket 2
D-287	API@60°F	37.6	40.7
D-93	Flash point, °F	<72	<72
D-86	Distillation, °F		
	IBP	200	119
	10%	320	234
	50%	460	451
	90%	668	652
	FBP	712	691
D-4294	Sulfur, wt %	0.125	0.124
D-97	Pour point	–38°F/–39°C	–38°F/–39°C
D-482	Ash, wt %	0.004	0.003
	Carbon, %	86.38	85.30
	Hydrogen, %	13.47	14.54
	Nitrogen, %	<0.1	<0.1
D-240	Heat content		
	Btu/lb	19,094	18,622
	Btu/gal	133,046	127,409

Troy Polymers Process for Glycolysis of PUFs

Troy Polymers, Inc. (TPI) has developed a patented glycolysis process (assigned to TPI and Polyventure, Inc.) for the conversion of mixed PUFs into polyol initiators (Figure 10). The process concept can recycle foam collected at shredders and convert the recovered PUF into polyol initiators, which can then be utilized to produce new urethane products (Figure 11).

Working with the Polyurethane Recycle and Recovery Council (PURRC), bench-tests to establish proof-of-concept were undertaken. The tests demonstrated the technical feasibility of the process in converting mixed clean PUFs from shredder residue to polyol initiators at a yield of about 88% (Table 4). Dirty foam was converted to polyol initiators at a yield of about 72%. However, the product from the dirty foam required more extensive filtration because of the solid residue contained within the foam.

Preliminary characterization of the products was also performed. The OH number, which is an indicator of molecular size (412 for the polyol initiator derived from clean foam and 570 for the polyol initiator derived from dirty foam), proves that the foam has been broken into smaller molecules. Commercially produced initiators can have OH numbers from about 100 to 1000 mg KOH/g. The OH numbers from the bench-test indicate that propoxylation of these intermediate products to produce polyols with OH numbers between 42 and 56 mg KOH/g, as commonly used in industry, is feasible. Obviously other characteristics of the polyols such as acid number, water content, color,

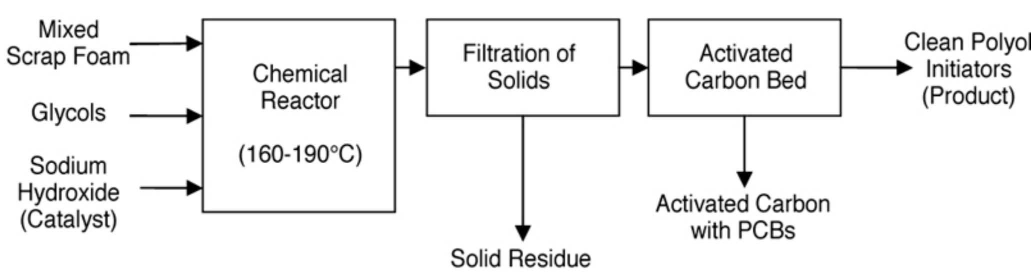

Figure 10. Glycolysis process conceptual process flow sheet.

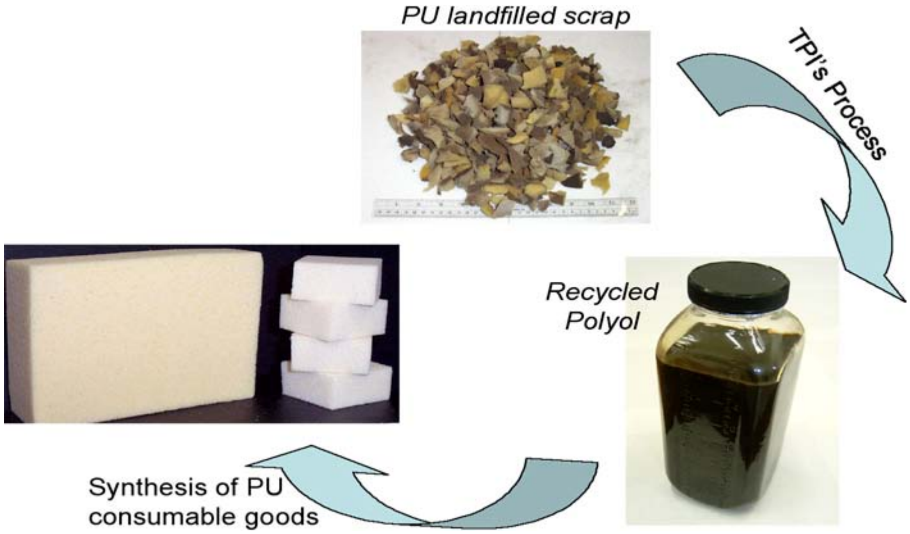

Figure 11. Glycolysis process concept.

Table 4. Glycolysis reaction input materials and product yield

Designation	Clean PUF	Dirty PUF
Starting Materials		
Diethylene glycol, g	1200	1200
NaOH, g	12.0	12.0
Foam scrap, g	1800	1800
Product yield		
Weight of products after glycolysis, g	2750	2762
Percent of recovered materials, %	91	92
Liquid fraction in products after filtration, %	96	79
Solid fraction (reside) in products after filtration, %	4	21
Yield of liquefied fraction, g	2640	2182
Yield of liquefied fraction (mass of liquid product)/ (mass of total input materials)*100	88	72
OH number (mgKOH/g)	412	570
Viscosity (cPs)		
• @23°C	350	500
• @50°C	200	300
• @77°C	100	—

pH, content of terminal unsaturation, acid and alkalinity content, amount of peroxide and carbonyl groups, amount of antioxidant and residual solvent, will have to be determined and controlled. The viscosity values of the polyol initiator products are also typical of the initiators used by industry. The greater viscosity of the product recovered from dirty foam indicates that further filtration of the product may be necessary.

As a result of this initial phase study, the CRADA team has agreed to fund a larger study at TPI. The study will include processing approximately 1,000 lb of dirty foam and produce about 50–100 gal of polyol for market evaluation. The polyurethane industry producers BASF, Bayer, and Dow have agreed to evaluate the polyol initiator product and identify potential applications.